ETHION AND FENITROTHION RESIDUES IN 'HAMLIN' ORANGE PEELS AND PULP DETERMINED BY GAS CHROMATOGRAPHY

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ABSTRACT

Residues of ethion and fenitrothion in 'Hamlin' orange peels and pulp were determined by gas chromotography in the State of São Paulo, Brazil. Samples were collected at different intervals after spraying.

Fenitrothion residues were more persistent than those of ethion on and in peels - degradation half-lives were 7 and 11 days for ethion and fenitrothion, respectively; persistence half-lives were 50 and 89 days. Residues of both insecticides were not detected into pulps.

INTRODUCTION

During the past several years, a substancial increase of Brazilian exports of concentrated citrus juice, fresh fruits, and citrus by-products has increased scientific interest on pesticide residue researches in relation to problems with international trade and local consumption.

The citrus crop in Southern Brazil has some critical entomological problems, mainly mites, fruit flies, scales, and aphids, which require rather extensive insecticide (acaricide) treatment programs every year, which include organophosphorus compounds. Ethion and fenitrothion are 2 recommended insecticides for the control of these pests.

GUNTHER *et alii* (1962) studied the behavior of ethion residues in 'Eureka' lemons and 'Valencia' oranges with the peels and pulps being analysed separately by an infrared spectrophotome

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tric procedure.

Our objectives were to establish degradation and persistence curves for residues of both compounds on and in peels and penetration into pulps of field-treated 'Hamlin' oranges and to correlate these residue levels with tolerance limits established by law.

MATERIALS AND METHODS

Field plot treatments

The experiment was conducted in a 7-year old 'Hamlin' orange variety orchard located at "Estação Experimental de Citricultura, Instituto Agronômico", in Cordeirópolis, State of São Paulo, Brazil.

At the beginning of the fruit ripening period, the insecticides were applied (March 9, 1979) at the following dosages: 400 ml ethion (10% AI plus 68% mineral oil) and 150 ml fenitrothion EC (50% AI) per 100 liters of water to the point of runoff using a Hatsuta portable motorized sprayer. The spreader-sticker Extravon 200 at 20 ml per 100 liters of water dosage was used for both insecticide sprays.

There were 3 replications for each insecticide with each 2 plants being considered as a replication.

Field sampling and laboratory processing

Samples of 16 full-sized fruits each were collected at 3, 10, 17, 24, 34, 45, 60, and 104-day intervals after spraying. Residues on and in the rind and in the pulp were determined separately. Samples were basically prepared according to GUNTHER (1969).

The procedure used was adapted from MOLLHOFF (1967). Duplicate subsamples of rinds or pulps were then extracted by blending them with acetone. The extracts were vacuum filtered and purified by solvent partition with chloroform and concentrated. Clean-up was performed in a Florisil column and elution proceeded with benzene. This solvent was removed by evaporation and the residue was dissolved in acetone for analysis.

Analysis

Samples were analysed by gas chromatography using an alkali flame phosphorus detector (AFID). The glass column was 180 cm in length and 2 mm i.d. packed with 10% DC 200 on 60/80 mesh silanized chromosorb W, and operated at 230°C with a nitrogen carrier gas flow rate of 30 ml/min. Hydrogen and air rates were 40 and 210 ml/min; injector and detector temperatures were 240° and 260°C; ethion and

fenitrothion retention times were approximately 8.5 and 3.5 minutes, respectively. Quantitation was by peak height times width at half height for ethion and by peak height for fenitrothion.

The method could detect residues of ethion as low as 0.01 ppm in the rind and pulp and residues of fenitrothion as low as 0.05 ppm in the rind and 0.02 ppm in the pulp. The recovery from pulp and rind fortified extracts was 92 - 104% for ethion and 82 - 102% for fenitrothion.

RESULTS AND DISCUSSION

Table 1 presents residues found on and in peels. Fig. 1 shows degradation and persistence curves for both rind insecticide residues.

TABLE 1 - Ethion and fenitrothion residues (ppm) in 'Hamlin' orange peels sprayed to runoff, March 9, 1979 (average of 3 replications).

Sampling time (days)	ethion	fenitrothion
3	4.64 ± 0.15	2.05 ± 0.06
10	2.25 ± 0.14	1.12 ± 0.07
17	2.18 ± 0.17	.96 ± 0.13
24	1.78 ± 0.11	.83 ± 0.10
34	1.42 ± 0.08	.73 ± 0.11
45	1.41 ± 0.21	.74 ± 0.06
60	.88 ± 0.04	.61 ± 0.10
104	.57 ± 0.09	.45 ± 0.03

Ethion residues in peels were approximately twice as much as those of fenitrothion up to 45 days after application and roughly the same at the end of field sampling period. Although less active ingredient of ethion than fenitrothion was applied per plant, the higher contamination level of the former 3 days after spraying may be accounted for by the mineral oil present in its formulation; the mineral oil helps to retain the active ingredient on the fruit's surface.

Based on Fig. 1, degradation half-lives were 7 and 11 days for ethion and fenitrothion, respectively; persistence half-lives

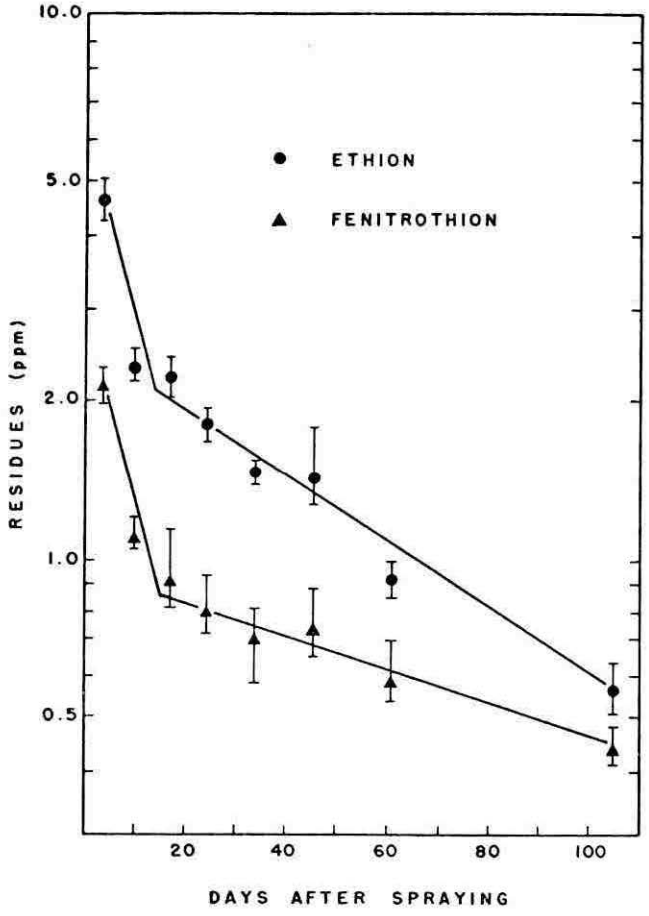

FIGURE 1 - Residual behavior of ethion and fenitrothion on and in peel of field-treated 'Hamlin' oranges.

were 50 and 89 days, indicating that fenitrothion residues were more persistent than those of ethion in peels. Climate and variety, mainly the former, affect pesticide residues behavior in citrus fruits (GUNTHER, 1969) and, possibly, these were the reasons for the different persistence half-life of 25 days for ethion residues from a similar formulation in 'Valencia' oranges found by GUNTHER *et alii* (1962).

There was no detection of residues into pulps at any sample collection day, indicating none or nondetectable residue penetration; thus, the rind functions as an efficient barrier against penetration of the residues (GUNTHER, 1969).

As 'Hamlin' oranges are 25.9 ± 1.5% rind by weight, whole-fruit residues can be approximated by taking 25% of the rind residue value. Thus, 3 days after application, ethion residues were below its tolerance value (2 ppm) and those of fenitrothion required 8 days to reach its tolerance limit (0.4 ppm).

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RESUMO

Resíduos de Ethion e Fenitrothion em Cascas e Polpa de Laranja 'Hamlin' Determinados por Cromatografia à Gás

Resíduos de ethion e fenitrothion em cascas e polpa de laranjas 'Hamlin' foram determinados por cromatografia à gás. As amostras foram coletadas a diferentes intervalos de tempo após a pulverização.

Os resíduos de fenitrothion foram mais persistentes do que

os de ethion em cascas - as meias-vidas de degradação foram 7 e 11 dias para ethion e fenitrothion, respectivamente; as meias-vidas de persistência foram de 50 e 89 dias. Os resíduos de ambos inseticidas não foram detectados nas polpas.